Comparison of Methods for Evaluating Ground-Contact Copper Preservative Depletion

Stan Lebow
Steven Halverson
U.S. Forest Service, Forest Products Laboratory
Madison, Wisconsin

ABSTRACT

Depletion of the biocide(s) used to treat wood has a major influence on service life and environmental concerns. However, little is known about the extent of depletion from the specific leaching method employed. Wood treated with two types of copper-based preservatives were leached using three different methods: field stakes (American Wood Protection Association (AWPA) method E7), laboratory soil exposure (AWPA method E20), or laboratory water immersion (AWPA method E11). Average losses tended to be greater from the field stakes than the small method E20 laboratory stakes, but this trend was difficult to substantiate because of the high variability with both methods. Little consistent relationship was observed between time of exposure and copper depletion in the field stakes, making it difficult to correlate the laboratory method with a specific duration of field exposure. Percentage of copper losses detected using AWPA method E11 appeared to be lower, and less variable, than those for either of the soil-contact leaching methods. The results of this study indicate that AWPA method E20 produces a range of leaching values more similar to field exposure than does AWPA method E11. All of these methods are intended to amplify and accelerate leaching, and therefore percentage depletion from commercial-size material would be substantially lower.

Keywords: soil contact, preservative leaching, method comparison

INTRODUCTION

Laboratory estimation of preservative loss from treated wood placed in ground contact is difficult. For decades, leaching small cubes by water immersion (AWPA method E11) was the only standardized laboratory method available for evaluating preservative loss in ground contact (AWPA 2007). However, water leaching is not clearly related to leaching of wood in soil contact and does not reflect the wide range of soil types and moisture conditions encountered in field exposures. Several studies have also indicated that leaching may be affected by the presence of soil components or by soil microorganisms (Crawford et al. 2002; Lebow et al. 2006b; Schultz et al. 2002). AWPA laboratory leachin g method E20 was developed in an attempt to partially account for the effect of soil properties on preservative leaching. The method involves burying small stakes in moist soil for 12 weeks (AWPA 2007). The extent of leaching is determined by assaying portions of the stakes before and after exposure. Method E20 greatly shortens the assessment of ground-contact leaching compared with related approaches based on field exposure of larger stakes. The smaller stake dimensions and the maintenance of saturated soil conditions are intended to accelerate loss of preservative. However, the extent of acceleration and the overall relationship between data obtained using the E20 method and that obtained using field stakes is unclear. In this study, we compared preservative losses from field stakes to those from AWPA method E20, using soil obtained from immediately adjacent to the field plot. For further comparison, leaching was also evaluated using AWPA method E11.

MATERIALS AND METHODS

Preservatives Evaluated

Two types of preservatives, with differing leaching characteristics, ,vere used to compare the leaching methods. One was chromated copper arsenate Type C (CCA-C), with an actives composition of 47.5% chromium (CrO_3 basis), 34.0% arsenic (As_2O_5 basis), and 18.5% copper (CuO basis). This formulation was evaluated with treatment solutions containing 1.0% actives (Table 1). CCA-C was selected as an established "fixed" or leach-resistant formulation. The other preservative evaluated was an alkaline borax-copper formulation (BC) currently used for field treatment of utility poles. BC (trade name CO-BOR) has an actives composition of 7.2% technical copper hydroxide and 92.8% sodium tetraborate decahydrate (10 mole borax). This formulation was evaluated with treatment solutions containing 1.4, 2.3, and 4.7% actives. BC was selected because it contains both a partially fixed component (copper) and an unfixed component (boron). In addition, the mechanism of copper fixation in BC is thought to differ from that in CCA and thus the leaching characteristics might also be expected to differ.

Table 1---Borate and copper concentrations in treatment solutions.

Treatment solution	Borax (%)	B_2O_3(%)	Cu as $Cu(OH)_2$ (%)	Cu as CuO (%)
1.4% BC	1.3	0.47	0.10	0.08
2.3% BC	2.2	0.80	0.14	0.11
4.7% BC	4.4	1.60	0.28	0.22
1% CCA-C	----	----	----	0.18

Specimen Preparation and Treatment

All specimens were cut from clear southern pine sapwood with between 2-5 growth rings per centimeter. Prior to treatment with the preservative, specimens were conditioned to ambient indoor conditions (6--10% moisture content).

Field stakes: For each treatment group, 25 stakes (19 by 19 by 610 mm) were sorted by density and assigned to treatment groups so that average density was uniform across all treatment groups. This provided 5 replicate stakes for removal at 1, 2, 3, 4, and 5 years of exposure. Following preservative treatment, a 152-mm section was cut from the end of each stake and reserved for assay of unleached preservative retention.

AWPA method E20 mini-stakes: 16 replicate small stakes (14 by 14 by 250 mm) were treated with each preservative solution. Following preservative treatment, a 100-mm section was cut from the end of each mini-stake and reserved for assay of unleached preservative retention.

AWPA method E11 cubes: For each treatment group, 30 leaching cubes (19 mm) were treated with each solution. Additional cubes were treated and reserved for determination of the unleached preservative retention. The 4.7% BC treatment solution was not evaluated using this method.

Treatment Conditions

All treatments were conducted using a full-cell pressure process. The initial vacuum was maintained at -75 kPa for 30 min; the pressure was maintained at 1.03 MPa for 1 h. The 2.3% and 4.7% BC treatments were done with solutions heated to approximately 50°C to improve solubi:ity, whereas the 1.4% BC treatments and CCA treatments were done at ambient temperature.

Following treatment, the specimens were close-stacked in plastic bags for one week, and then allowed to air-dry under room conditions. Sections were cut from the ends of field stakes and small laboratory stakes for assay of the original treatment retention (Table 2).

Table 2 ----Average borate and copper retentions in specimens (by assay) prior to exposure.

	Borate retention as B_2O_3 (kg/m^3)			Copper retention as CuO (kg/m^3)		
Preservative formulation (%)	Field stakes	AWPA method E20 small stakes	AWPA method E11 cubes	Field stakes	AWPA method E20 small stakes	AWPA method E11 cubes
1.4 BC	2.86	1.95	2.23	0.43	0.33	0.35
2.3 BC	4.35	3.56	3.56	0.71	0.39	0.50
4.7 BC	8.89	8.59	Not tested	1.51	0.83	Not tested
1 CCA	----	----	----	1.10	0.83	0.72

Leaching Exposures

Field Stakes: The Wisconsin plot is located in an open field a few miles west of Madison, Wisconsin. The plot has a clay loam soil and receives an average of 780 mm of precipltation each year. The stakes were placed in rows with 305-mm spacing between stakes within each row and 915 mm between rows. The stakes were randomly assigned locations within the plot and were buried vertically to one-half their length. Five replicate stakes were removed at 1, 2, 3, 4, and 5 years after installation. After drying in the laboratory, 50-mm long sections of each stake were removed from 50 mm below the ground-line and assayed to determine the retention of the remaining preservative. The preservative content in the exposed stakes was compared to that in the corresponding section removed from the stake prior to installation.

AWPA method E20 laboratory stakes: The soil used in this test was removed from directly adjacent to the field-exposure plot. The method used was similar to that described in AWPA method E20 except that 16 replicates per treatment group were used, and 10 replicate stakes were placed into each container. The soil was initially saturated, allowed to drain for 16 h, and then the stakes were buried vertically so that their tops were flush with the surface of the soil. The containers were weighed to determine their initial weight, and three times per week water was added, as needed, to maintain this initial weight. After 12 weeks, the stakes were removed from the soil and allowed to air-dry. A 70-mm long section was cut from the center of the stakes and assayed to determine the retention of the remaining preservative. The preservative content in the exposed stakes was compared to that in the in the corresponding section removed from the stake prior to exposure.

AWPA method E11 cubes: Six cubes were placed into each of 5 replicate leaching containers and immersed in 300 mls of deionized water. Immediately upon immersion, the leaching container was subjected to a vacuum to withdraw the air from the wood and saturate the cubes with the leaching water. The containers were then subjected to mild agitation to ensure water movement. After 6 h, all the water in the container was drained off the cubes and collected for analysis. It was replaced with an equivalent amount of fresh deionized water, and agitation was resumed. This process was repeated at 24 h, 48 h, and subsequently at 48-h intervals until the cubes had been leached for a total of 336 h (2 weeks). A subset of treated but unleached cubes was milled and analyzed to determine the initial concentration of preservative in the blocks. Percentage copper loss was calculated by comparing the sum of copper content in the leachate to that in the unleached blocks.

RESULTS AND DISCUSSIONS

Copper losses from the field-stake exposures and laboratory stake trials were highly variable, especially for the BC treatments (Table 3). This variability is most evident for the field stakes, where losses of copper often appeared higher after 1 year than after 5 years of exposure (Figure 1).

Table 3----Average percentage of preservative elements remaining in specimens after exposure. Values in parentheses represent one standard deviation from the mean.

Preservative and element	Field stakes remaining at year (%) 1	2	3	4	5	AWPA method E20 total remaining (%)	AWPA method E11 total remaining (%)
CCA-Cu	75 (14)	97 (8)	85 (6)	81 (12)	81 (10)	84 (5)	88 (1)
1.4% BC- Cu	61 (13)	82 (9)	62 (8)	54 (6)	80 (8)	81 (18)	92 (0)
2.3% BC- Cu	71 (17)	91 (4)	81 (8)	58 (32)	74 (23)	82 (30)	90 (0)
4.7% BC- Cu	82 (19)	87 (9)	88 (13)	51 (11)	83 (13)	85 (18)	Not tested
1.4% BC- B	2 (1)	5 (8)	7 (4)	2 (1)	1 (1)	8 (7)	- 13 (2)
2.3% BC- B	2 (0)	0(0)	2 (2)	1 (1)	0(0)	5 (4)	5 (2)
4.7% BC- B	2 (1)	9 (16)	6 (12)	1 (0)	0(0)	2 (1)	Not tested

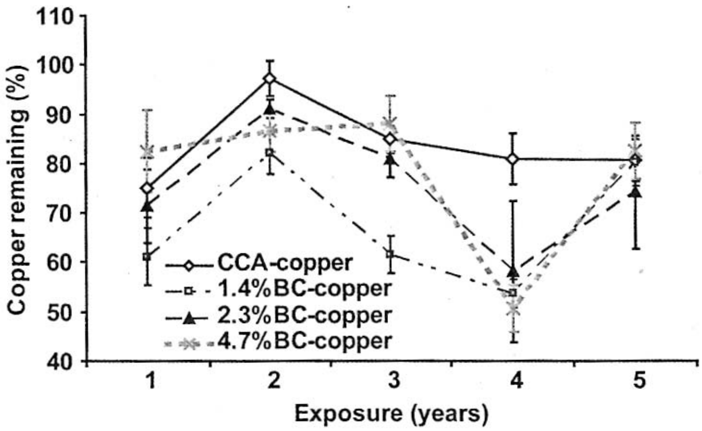

Figure 1. Average percentage copper remaining in below-ground portions of field stakes at each year of exposure. Bars show plus or minus one standard error.

It is possible that most of the poorly fixed copper was lost during the first year of exposure and that the smaller copper losses in subsequent years were masked by the method variability. Losses of boron were less variable, probably because virtually all boron was lost within one year of stake exposure. Substantial variability is often associated with "before and after" sampling of treated wood to evaluate leaching because of the variability associated with distribution of preservative within test specimens and with preparation of wood samples for assay (Lebow et al. 2006a). With the field-exposure stakes, this problem was exacerbated by the relatively small number of replicates (5) and possibly by the variability associated with soil-exposure conditions within the test plot. Variability was almost as great for the smaller stakes exposed under laboratory conditions, although standard errors were lower because of the larger number of replicates (Figure 2). In every case, the variability associated with copper losses from CCA-treated wood appeared to be less than that for the BC treatments, but this effect may be an anomaly. In contrast to the soil exposure methods, variability associated with copper losses evaluated by the AWPA E11 method was low. Low variability associated with this procedure is attributable to several factors, including uniformity of treatment in the small cubes, grouping of 6 cubes into one leaching container, and analysis of low concentrations of preservative in water rather than high concentrations of preservative in wood.

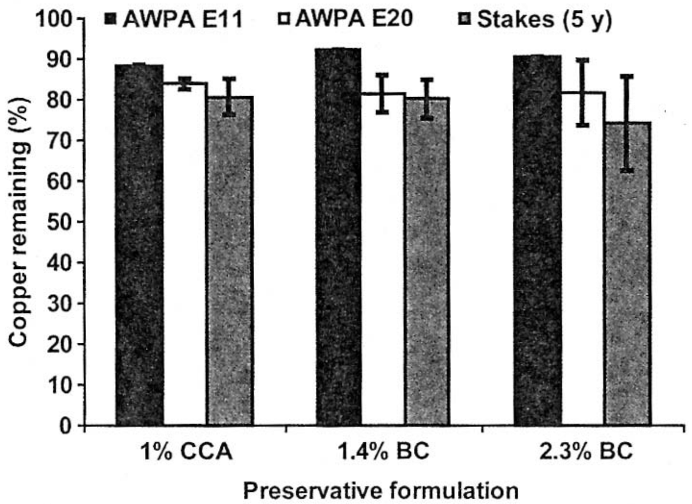

Figure 2. Average percentage copper remaining in specimens at conclusion of test (year 5 losses for field stakes). Bars show plus or minus one standard error.

Although the AWPA E11 method has the advantage of short duration and low variability, its relationship to leaching from wood in ground contact is not obvious. The E11 method is often considered unrealistically rigorous because the small cubes have a high proportion of exposed end-grain. In our study, however, copper losses from both the AWPA method E20 small stakes and from the field stakes appeared to be equivalent to or greater than losses detected using AWPA method E11. This may be a result of the longer duration of the two soil-contact leaching exposures, or the effect of soil components on leaching of copper, or both. A previous study indicated that copper losses from small stakes exposed in soil were greater than those from small stakes immersed in water (Crawford et al. 2002). Copper losses for field stakes in this study do not appear to be excessive. A previous study reported copper losses of over 30% for CCA-treated 19- by 19-mm stakes exposed for 55 or 66 months at test sites in Mississippi (Schultz et al. 2002).

One of the objectives of this study was to relate the results of the AWPA E20 laboratory method to losses from the field-exposure stakes. This comparison is difficult because of the high variability experienced with both methods, and because of the lack of a consistent "years of exposure" effect in the field stakes. However, in an effort to relate the two methods, we have regressed the percentage of remaining copper against years of exposure for the field stakes (Figure 3). In this regression, we forced the *y*-intercept to occur at 100% because by definition 100% of the preservative is present before exposure. Note that forcing the *y*-intercept to occur at 100% created a somewhat misleading relationship between copper loss and time of exposure (compare Figures 2 and 3). Plotting the remaining copper content for the AWPA E20 laboratory stakes against the linear relationships for the field-exposure stakes indicates that the copper losses using AWPA E20 method were equivalent to between 2 to 3 years of exposure for the BC-treated stakes and between 3 to 4 years of exposure for the CCA-treated stakes. However, the relationship between years of exposure and copper losses from the field stakes is very weak, and variability associated with both methods makes it difficult to compare copper losses between the two methods.

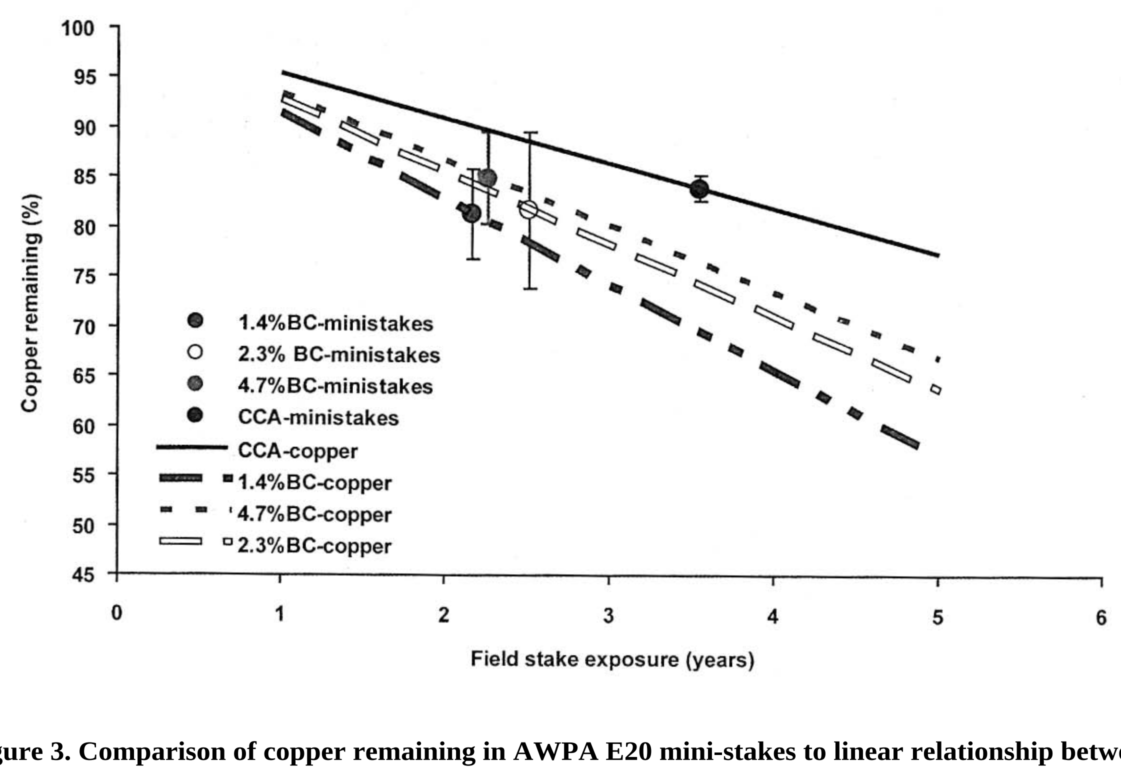

Figure 3. Comparison of copper remaining in AWPA E20 mini-stakes to linear relationship between years of exposure and copper remaining in field stakes.

CONCLUSIONS

Substantial variability in copper loss was associated with both the field stakes and the AWPA E20 method. Average total copper losses for both types of preservatives tended to be greater from the field stakes than the method E20 laboratory stakes, but this trend is difficult to substantiate because of variability associated with both methods. Because little or no consistent relationship was observed between time of exposure and copper depletion in the field stakes, we were not able to confidently equate the losses from method E20 to a specific duration offield exposure. Percentage copper losses detected using water leach by AWPA method E11 appeared to be lower and less variable than those for either of the soil-contact leaching methods. This study indicates that for the two types of preservatives evaluated, AWPA method E20 produces a range of copper leaching values more similar to field exposure than does AWPA Method E11. All three methods are intended to amplify and accelerate leaching, and percentage depletion from commercial-size material would be substantially lower.

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